

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. : 10/719,381
Applicant (s) : Cady et al.
Filed : November 20, 2003
TC/A.U. : 1713
Examiner : R.D. Harlan
Title : SHEAR THINNING ETHYLENE/ α -OLEFIN INTERPOLYMERS
AND THEIR PREPARATION

Docket No. : DW0029USCNT
Customer No. : 00109

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R § 1.132

I, MORGAN M. HUGHES, declare and state the following:

- (1) I am a Senior Technology Specialist in the Polyolefins Group of the Polyolefins and Elastomers Research and Development Laboratory at The Dow Chemical Company, B-1470 Building, Freeport, Texas, 77541.
- (2) I received a Masters of Science degree in Chemistry from Colorado State University in 1981.
- (3) I am currently an employee of The Dow Chemical Company ("DOW"), and began my employment at DOW, as a research chemist, in 1981. I joined a DOW – DuPont joint venture in 1996, and returned to DOW in 2005. I have worked in the area of polymer synthesis and characterization, and I am familiar with the properties of polyolefins prepared from different types of catalysts, such as constrained geometry catalysts, metallocene catalysts and Ziegler-Natta type catalysts. I have studied polyolefin resins and polymerization processes for 20+ years.

- (4) I have examined U.S. Patent 4,343,755 to Miller et al. (hereinafter the '755 patent). I received two ethylene/1-butene copolymers that were prepared in accordance with the description set forth in the accompanying Declaration from Robert J. Jorgensen, filed in the above-identified application. These two copolymers are designated "Copolymer 1" and "Copolymer 2," respectively. Copolymer 1 was produced from Run 1, and Copolymer 2 was produced from Run 2, each as described in the Jorgensen Declaration.
- (5) I have examined the Mooney Viscosities for Copolymer 1 and Copolymer 2 at the following temperatures, 150°C (ML_{1+4} @ 150°C), 160°C (ML_{1+4} @ 160°C) and 170°C (ML_{1+4} @ 170°C), in accordance with ASTM D-1646-04 (instrument: Mooney Model MV2000E). Mooney Viscosities at 140°C, and lower, could not be accurately measured due to the crystallization of each copolymer. Crystallization was observed for each polymer at 140°C. For each copolymer, an estimated Mooney Viscosity at 125°C was determined from a linear extrapolation of the plot of Mooney Viscosity (at 150°C, 160°C and 170°C) versus inverse temperature ($1/T$ ($^{\circ}C^{-1}$)), as shown in Figure 1, attached herewith. It is estimated that the actual Mooney Viscosity for each copolymer at 125°C is higher than the extrapolated value, since at such low temperature, these copolymers are significantly, if not completely, crystalline, and thus, in a highly viscous, solid state.
- (6) The measured Mooney Viscosities and the extrapolated viscosities are shown in Table 1 below. Copolymers 1 and 2 were compared against an ethylene-propylene-diene (EPDM) polymer control. The molecular weight distribution, MWD, for each copolymer was determined from Gel Permeation Chromatography, GPC, data, using a Polymer Laboratories Model PL-GPC210.

Table 1

Copolymer	MWD	Mooney Viscosity @ 125°C	Mooney Viscosity @ 150°C	Mooney Viscosity @ 160°C	Mooney Viscosity @ 170°C
1	4.37	11.8*	7.8	6.4	5.4
2	4.02	22.9**	15.8	12.7	11.5
Control	3.21	18.8	13.7	-	-

* Extrapolated value from $(MV @ T) = 3063.9(1/T) - 12.666$ ($R^2 = 0.9964$)

** Extrapolated value from $(MV @ T) = 5520.9(1/T) - 21.262$ ($R^2 = 0.955$)

- (7) The viscosity of each copolymer (Copolymer 1 and Copolymer 2) was measured in poise (dyne-second/square centimeter (d-sec/cm²)), at 190°C, at shear rates within a range from 0.1 radian per second to 100 radian per second, under a nitrogen atmosphere, using an Advanced Rheometrics Expansion System, a dynamic mechanical spectrometer. The viscosities at 0.1 rad/sec and 100 rad/sec are represented, respectively, as $V_{0.1}$ and V_{100} . Again these two copolymers were compared against the control, as discussed above. The viscosity results are shown in Table 2 below.

Table 2

Copolymer	Viscosity at 0.1 rad/sec @ 190°C ($V_{0.1}$) (Poise)	Viscosity at 100 rad/sec @ 190°C (V_{100}) (Poise)	$V_{0.1}/V_{100}$
1	6638	1404	4.728
2	16629	2116	7.859
Control	40449	1261	32.08

- (8) The viscosity ratio, $V_{0.1}/V_{100}$, also referred to as “RR,” which stands for Rheology Ratio, is the ratio of the viscosity at 0.1 rad/sec to the viscosity at 100 rad/sec, each as discussed above. The RR values for the two copolymers and the control are shown in Table 2 above. The Rheology Ratio, provides an indication of the shear thinning behaviour of the polymer, and this ratio increase as the polymer shows less resistance to shear forces at higher shear rates (for example, at 100 rad/sec). A polymer with higher levels of long chain branching typically show significant decrease in resistance to shear forces at higher shear rates. As the amount of long chain branching in a polymer increases, the RR value increases. Thus, the RR value is an indication of the amount of long chain branching in a polymer, with a higher RR value indicating a higher level of long chain branching.
- (9) Claim 1 of the above-identified application provides an equation for determining the “Process Rheology Ratio” or “PRR” of a polymer. This equation is set out below in Equation 1:

$$\text{PRR} = V_{0.1}/V_{100} + [3.82 - (\text{ML}_{1+4} \text{ at } 125^{\circ}\text{C})] \times 0.3 \quad (\text{Eqn. 1}).$$

For a comparison of polymers with equal molecular weight characteristics (Mw, Mn and MWD), the $V_{0.1}/V_{100}$ ratio would provide a very close (almost direct) measure of the degree of long chain branching. For polymers with different molecular weight characteristics, the correction factor $\{[3.82 - (\text{ML}_{1+4} \text{ at } 125^{\circ}\text{C})] \times 0.3\}$ was developed to account for the effects of molecular weight and molecular weight distribution.

- (10) The calculated PRR values for copolymers 1 and 2 and the control are listed in Table 3 below. Each PRR value was calculated, using Equation 1, from the $V_{0.1}/V_{100}$ ratio and the Mooney Viscosity @ 125°C. As shown in Table 3, the PRR value for copolymer 1 and the PRR value for Copolymer 2 are both less than 4. The calculated PRR value for each of Copolymer 1 and Copolymer 2, as shown in Table 3, is estimated to be higher than the PRR value that could

be calculated, if the viscosity of each copolymer could be measured at 125°C,
as opposed to extrapolated at 125°C.

Table 3

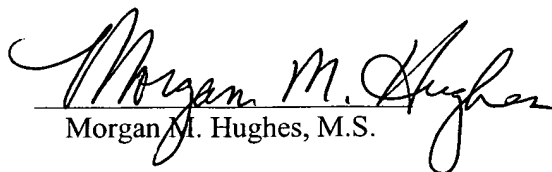
Copolymer	Mooney Viscosity @ 125°C	V _{0.1} /V ₁₀₀	PRR
1	11.8*	4.728	2.334
2	22.9**	7.859	2.135
Control	18.8	32.08	27.59

*Extrapolated

**Extrapolated

The undersigned declares further that all statements made herein of his own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements, and the like, so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date August 15, 2006


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Mooney Viscosity vs 1/Temperature

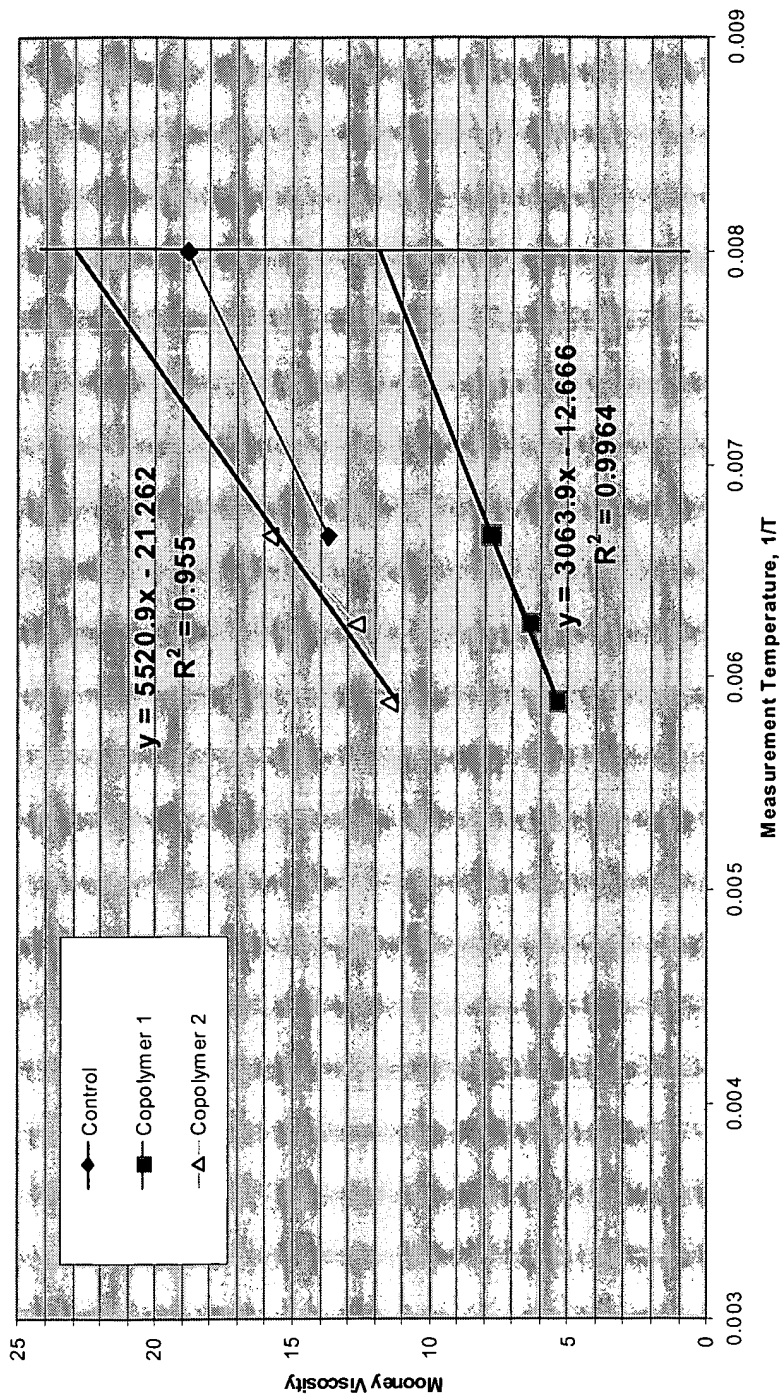


FIGURE 1